

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

08/30/00

Applicant(s): Brian A. Vaartstra

Docket No.: 150.00800102

Title: SUPERCRITICAL COMPOSITIONS FOR REMOVAL OF ORGANIC MATERIAL AND METHODS OF USING SAME

16962 US 51702  
08/30/00

Commissioner for Patents  
 ATTN: Box Patent Application  
 Washington, D.C. 20231

We are transmitting the following documents along with this Transmittal Sheet (which is submitted in triplicate):

Copy of Utility Patent Application: Specification (17 pgs); Claims (42 claims on 7 pgs); 1 pg Abstract, 3 sheets of informal drawings.

Copies of signed Declaration (2 pgs.) and Election and Power of Attorney (1 pg.), both as filed in prior application.

A return postcard.

Other: Request for Filing A Divisional Patent Application Under Rule 1.53(b) (3 pgs.); Preliminary Amendment (4 pgs.).

A check in the amount of \$690 to cover the filing fee, which is calculated below:

APPLICATION FILING FEE					
	Number of Claims Filed (1)	Claims Included in Basic Filing Fee (2)	Number of Extra Claims (1-2)	Cost per Extra Claim	Fee Required
Total Claims	14	-20 =	0	x \$18 =	0
Independent Claims	3	-3 =	0	x \$78 =	0
One or More Multiple Dependent Claims Presented? If Yes, Enter \$260 Here					0
Enter Basic Filing Fee (Utility Patent-\$690/Design Patent-\$310) Here →					\$690
Total Application Filing Fee					\$690

Please consider this a PETITION FOR EXTENSION OF TIME for a sufficient number of months to enter these papers and please charge any additional fees or credit overpayment to Deposit Account No. 13-4895. Triplicate copies of this sheet are enclosed.

MUETING, RAASCH & GEBHARDT, P.A.  
 P.O. Box 581415, Minneapolis, MN 55458 (612-305-1220)

By: *Ann M. Mueting*  
 Name: Ann M. Mueting  
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## CERTIFICATE UNDER 37 CFR §1.10:

"Express Mail" mailing label number: EL542402278US

Date of Deposit: August 30, 2000

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR §1.10 on the date indicated above and is addressed to the Commissioner for Patents, ATTN: Box Patent Application, Washington, D.C. 20231.

By: *Anne M. Richards*  
 Name: *Anne M. Richards*

(LARGE ENTITY TRANSMITTAL UNDER RULE 1.10)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Docket Number	Anticipated Classification		Prior Application	
	Class	Subclass	Examiner	Art Unit
150.00800102			N. Barreca	1756

**REQUEST FOR FILING A DIVISIONAL PATENT APPLICATION  
UNDER RULE 1.53(b)**

109862 U.S. PTO  
09/28/02  
09/28/02



Commissioner for Patents  
Attn: Box Patent Application  
Washington, D.C. 20231

Sir:

This is a request for filing a divisional application under 37 CFR §1.53(b) of Serial No. 09/141,866, filed on August 28, 1998, entitled SUPERCRITICAL COMPOSITIONS FOR REMOVAL OF ORGANIC MATERIAL AND METHODS OF USING SAME by the following inventor(s) (name, address, and citizenship):

**Brian A. Vaartstra  
3417 Braden Lane  
Nampa, ID 83686  
Citizenship: Canada**

1.  Enclosed is a copy of the specification (including claims, abstract, and drawings) as filed in the prior application.
2.  Enclosed is a new specification (including claims and abstract). The entire disclosure of the prior application is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference.
3.  Enclosed are copies of the Declaration and Election and Power of Attorney, both filed in the prior application.
4.  Enclosed is a newly executed Declaration and Power of Attorney.
5.  Enclosed are formal drawings (\_\_\_\_ sheets).
6.  Cancel in this application original claims 1-18 and 33-42 of the prior application before calculating the filing fee. (At least one original independent claim must be retained for filing purposes.)

7.  A preliminary amendment is enclosed (the filing fee calculation includes any new claims). (Claims added by this amendment have been properly numbered consecutively beginning with the number next following the highest numbered original claim in the prior application.)

8.  The filing fee is calculated below:

CLAIMS AS FILED			
NUMBER FILED	NUMBER EXTRA	RATE	BASIC FEE \$690
Total Claims 14-20 =	0	\$18	0
Independent Claims 3-3 =	0	\$78	0
MULTIPLE DEPENDENT CLAIM PRESENTED		\$260	0
FILING FEE:			<b>\$690</b>

9.  A Verified Statement that this filing is by a small entity (37 CFR §§1.9, 1.27, 1.28) is:

already filed in the parent application.

attached.

10.  A check in the amount of \$690 is attached.

11.  The Commissioner is hereby authorized to charge any additional fees as set forth in 37 CFR §1.16 to 1.18 which may be required by this paper or credit any overpayment to Account No. 13-4895.

12.  This application is being filed by less than all of the inventors named in the prior application. Please delete the names of the following inventor(s) who are not inventors of the invention claimed in the present application:

13.  Amend the specification by inserting as the first sentence on page 1, the following: -- This is a division of application Serial No. 09/141,866, filed on August 28, 1998, (pending), which is incorporated herein by reference.--

14.  Priority of foreign application Serial No. \_\_\_, filed on \_\_\_ in (country) \_\_\_\_\_ is claimed under 35 U.S.C. §119.

15.  The prior application is assigned of record to Micron Technology, Inc.

Filed: Herewith

Title: SUPERCritical COMPOSITIONS FOR REMOVAL OF ORGANIC MATERIAL AND METHODS OF USING SAME

16. X The Power of Attorney in the prior application is to:

Mueting, Raasch & Gebhardt, P.A.  
P.O. Box 581415  
Minneapolis, MN 55458-1415

**Address all future communications to:**

MUETING, RAASCH & GEBHARDT, P.A.  
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Date: August 30, 2000

Ann M. Mueting

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Date of Deposit August 30, 2000

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Anne M. Richards  
Name: Anne M. Richards

PATENT  
Docket No. 150.00800102

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Brian A. VAARTSTRA ) Group Art Unit: Unknown  
  )  
Serial No.: Unassigned ) Examiner: Unknown  
  (Parent: 09/141,866)  
  )  
Filed: Herewith )  
  (Parent: August 28, 1998) )

For: SUPERCRITICAL COMPOSITIONS FOR REMOVAL OF ORGANIC  
MATERIAL AND METHODS OF USING SAME

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**PRELIMINARY AMENDMENT**

Commissioner for Patents  
ATTN: BOX PATENT APPLICATION  
Washington, D.C. 20231

Dear Sir/Madam:

Prior to taking up the above-identified application for examination, please amend the application as follows:

**In the Specification**

Please amend the specification as follows:

At page 14, line 18, please delete "apparatus" and insert –mixing manifold– therefore.

At page 14, line 23, please insert "mixing" before "manifold".

**In the Claims**

Please cancel claims 1-18 and 33-42 as indicated in the Request for Filing a Divisional Application filed herewith. The pending claims are reproduced herein for the Examiner's convenience.

19. An organic material removal composition comprising at least one component in a supercritical state, wherein the composition includes an oxidizer selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>).

20. The composition of claim 19, wherein the at least one component in a supercritical state is the oxidizer selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>).

21. The composition of claim 20 wherein the at least one component in a supercritical state is sulfur trioxide.

22. The composition of claim 21, wherein the composition consists essentially of sulfur trioxide in the supercritical state.

23. The composition of claim 19, wherein the composition includes a supercritical component in the supercritical state selected from the group of carbon dioxide (CO<sub>2</sub>), ammonia (NH<sub>3</sub>), H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), nitrogen (N<sub>2</sub>), helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe).

24. The composition of claim 23, wherein the supercritical component is carbon dioxide and the oxidizer is sulfur trioxide.

25. An organic material removal composition comprising an oxidizer in a supercritical state, wherein the oxidizer is selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>).
26. The composition of claim 25, wherein the oxidizer is sulfur trioxide.
27. An organic material removal composition comprising:
  - a first component selected from the group of carbon dioxide (CO<sub>2</sub>), ammonia (NH<sub>3</sub>), H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), nitrogen (N<sub>2</sub>), helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe), wherein the first component is in a supercritical state; and
  - a second component selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>).
28. The composition of claim 27, wherein the first component is carbon dioxide.
29. The composition of claim 27, wherein a ratio of the first component to the second component in the supercritical state is in the range of about 1:100 by volume to about 100:1 by volume.
30. The composition of claim 27, wherein the second component is sulfur trioxide and the first component is carbon dioxide.
31. The composition of claim 30, wherein a ratio of carbon dioxide:sulfur trioxide is preferably in the range of about 10:1 by volume to about 1:1 by volume.

*Serial No. Unknown (Parent Serial No. 09/141,866)*

*Filed: Herewith (Parent: August 28, 1998)*

*Title: SUPERCRITICAL COMPOSITIONS FOR REMOVAL OF ORGANIC MATERIAL AND METHODS OF USING SAME*

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32. The composition of claim 30, wherein the sulfur trioxide is in a supercritical state.

**Remarks**

Please enter and consider claims 19-32. The specification has been amended as requested by the Examiner in connection with the prior application. No new matter is introduced.

**Conclusion**

The Examiner is invited to contact Applicant's Representatives, at the below-listed telephone number, if there are any questions regarding this Preliminary Amendment or if prosecution of this application may be assisted thereby.

Respectfully submitted,  
Brian A. VAARTSTRA,  
By his Representatives,  
Muetting, Raasch & Gebhardt, P.A.  
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Date

*August 30, 2000*

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"Express Mail" mailing label number EL542402278US

Date of Deposit August 30, 2000

I hereby certify that this paper and/or fee is/are being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Attn: Box Patent Application, Washington, D. C. 20231

*Anne M. Richards*  
Name: Anne M. Richards

Patent  
Docket No. 150.0080 01 01

**SUPERCRITICAL COMPOSITIONS FOR REMOVAL  
OF ORGANIC MATERIAL AND METHODS OF USING SAME**

### **Field of the Invention**

The present invention relates to the treating of surfaces of an object, e.g.,  
treating of wafer surfaces in the fabrication of semiconductor devices. More  
particularly, the present invention relates to removal of organic material, e.g.,  
etching or cleaning of resists, organic residues, etc., from surfaces using  
supercritical compositions including an oxidizer.

## Background of the Invention

15 Removal of organic materials (e.g., stripping of photoresist used for fabrication of semiconductor devices, cleaning of organic residues from surfaces of objects or structures, removal of polymers from crevices or grooves of structures or from other difficult regions of a structure, etc.) is one of various steps required in the production of semiconductor devices or other objects such as flat panel displays.

20 For example, whenever photoresist or other organic masks are used, removal of organic material is typically necessary.

The removal of photoresist or other organic material is usually performed by either a dry or wet removal method. Wet removal techniques generally involve the use of specialized oxidizing solutions such as sulfuric acid and hydrogen peroxide solutions. Wet removal generally refers to the contact of a surface with a liquid chemical solution. For example, material is removed as an agitated liquid or spray passes over the surface. Dry etching refers to the contact of a surface with a gaseous plasma composition. Dry removal techniques generally remove organic material using oxygen plasmas, e.g., oxygen ash techniques, and possibly with hydrogen plasma assistance.

Removal of photoresist or other organic material from complex structures is typically done in an oxygen plasma ash tool or with a multiple step wet strip process, or combinations thereof. However, for example, as semiconductor device structure geometries and other structure geometries continue to get smaller, e.g., into the submicron range such as below 0.25 micron, neither conventional dry removal nor wet removal techniques provide adequate removal of organic material during the processing of such complex structures without damaging the structure being produced. For example, with device structures having critical dimensions below 0.25 micron geometries, conventional techniques may not be adequate for removal of organic material such as ultraviolet (UV) radiation hardened photoresist and/or sidewall deposited resist or residue, nor adequate for removal of organic material such as organic residue in difficult crevices or grooves of such device structures.

Various processing steps produce problems for the removal of organic material, e.g. photoresist. For example, surface hardening of photoresist due to reactive ion etching (REI) or ion implantation processes increases the difficulty in such removal. Further, for example, post formation bakes and UV curing steps may cause chemical changes in the photoresist that may cause difficulty in removal of the resists.

Both wet and dry organic removal techniques may not provide adequate removal when organic materials are present in complex structures, such as high aspect ratio openings, including submicron grooves, narrow crevices, etc. Wet stripping techniques do not appear to overcome such problems and generally result in incomplete photoresist removal. For example, both grooves and crevices render wet stripping solutions ineffective by limiting the solvent access to the organic material to be removed by reason of surface tension and capillary actions.

Dry techniques may also fail to completely remove such organic material in grooves and crevices, particularly due to the polymer formed on sidewalls of the resist. Dry plasma etching also appears to result in incomplete removal. For example, sidewall polymer formations may occur as a result of the interaction of

released by-products of plasma etching with the sidewalls of the structure. Such polymers are not easily removed using ashing processes.

While wet etchants have many preferable characteristics as compared to dry etchants, dry etchants can be used in fabrication processes without the need to dry the structure being processed after a dry organic material removal step has been performed. The added step of drying the structure that is required when using a conventional wet etchant adds to the cost of fabrication. A lack of full process automation may also result from the added step of drying the structure. Another advantage of etching with a dry etchant is that it often decreases the safety hazards associated with wet removal solutions due to the relatively small amount of chemicals utilized in the dry etchant, e.g., environmentally advantageous.

Supercritical fluids have been used to remove organic residue from a variety of surfaces or extract substances from various materials. A gas is determined to be in a supercritical state (and is referred to as a supercritical fluid) when it is subjected to a combination of pressure and temperature so that its density approaches that of a liquid (i.e., the liquid and gas state coexist). For example, supercritical fluids have been used to clean contact lenses by etching residue from lens surfaces, as disclosed by Bawa et al. in PCT Application Publication Number WO 95/20476. Further, supercritical carbon dioxide (CO<sub>2</sub>), has also been used to remove exposed organic photoresist films, as disclosed by Nishikawa et al. in U.S. Patent No. 4,944,837.

It is also known that organic material is removed rather well by certain oxidizing gases, in particular, sulfur trioxide. For example, as described in U.S. Patent No. 5,037,506 to Gupta et al., entitled "Method of Stripping Layers of Organic Materials," issued 6 August 1991, gaseous sulfur trioxide is used to remove various organic coatings, polymerized photoresist, and implant and deep-UV hardened photoresist layers during the manufacture of semiconductor or ceramic devices. Further, for example, as described in U.S. Patent No. 4,778,536 to Grebinski, entitled "Sulfur Trioxide Vapor Phase Stripping" issued 18 October

1988, water vapor is contacted with sulfur trioxide vapor adjacent the surface of an object to provide a hot mixture comprising sulfur trioxide, water, and sulfuric acid to remove photoresist.

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### Summary of the Invention

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Compositions and methods are needed which achieve effective removal of organic materials. For example, effective removal is required in many circumstances, such as, in high aspect ratio geometries, complex structures, when side wall polymerization occurs as a result of an etching process, when resist is UV hardened, etc. The present invention provides compositions and methods for achieving such removal.

15

A method for removing organic material in the fabrication of structures according to the present invention includes providing a substrate assembly having an exposed organic material and removing at least a portion of the exposed organic material using a composition having at least one component in a supercritical state. The composition includes an oxidizer selected from the group of sulfur trioxide ( $\text{SO}_3$ ), sulfur dioxide ( $\text{SO}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), NO,  $\text{NO}_2$ , ozone ( $\text{O}_3$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ),  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and oxygen ( $\text{O}_2$ ). For example, the exposed organic material may be selected from the group of resist material, photoresist residue, UV-hardened resist, X-ray hardened resist, carbon-fluorine containing polymers, plasma etch residues, and organic impurities from other processes.

20

In one embodiment of the method, the at least one component in a supercritical state is an oxidizer selected from the group of sulfur trioxide ( $\text{SO}_3$ ), sulfur dioxide ( $\text{SO}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), NO,  $\text{NO}_2$ , ozone ( $\text{O}_3$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ),  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and oxygen ( $\text{O}_2$ ); preferably sulfur trioxide.

25

In another embodiment of the method, the composition includes a supercritical component in a supercritical state selected from the group of carbon dioxide ( $\text{CO}_2$ ), ammonia ( $\text{NH}_3$ ),  $\text{H}_2\text{O}$ , nitrous oxide ( $\text{N}_2\text{O}$ ), carbon monoxide (CO), inert gases (e.g., nitrogen ( $\text{N}_2$ ), helium (He), neon (Ne), argon (Ar), krypton (Kr),

and xenon (Xe); preferably carbon dioxide.

In yet another embodiment of the method, the supercritical component is carbon dioxide and the oxidizer is sulfur trioxide.

An organic material removal composition according to the present invention includes a composition having at least one component in a supercritical state. The composition includes an oxidizer selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>).

In one embodiment of the composition, the at least one component in a supercritical state is the oxidizer selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>); preferably sulfur trioxide.

In another embodiment of the composition, the composition includes a supercritical component in the supercritical state selected from the group of carbon dioxide (CO<sub>2</sub>), ammonia (NH<sub>3</sub>), H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), inert gases (e.g., nitrogen (N<sub>2</sub>), helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe); preferably carbon dioxide.

In another method according to the present invention for use in fabricating a semiconductor structure, the method includes providing a pressurizable chamber and introducing at least one component of a composition into the chamber. A substrate assembly having exposed organic material is positioned within the chamber. The pressure and temperature of the chamber is controlled for maintaining the at least one component of the composition in a supercritical state. The composition includes an oxidizer selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>). At least a portion of the organic material is removed from the substrate assembly using the composition having the at least one component in the supercritical state.

In one embodiment of the method, the at least one component in a

supercritical state is an oxidizer selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>); preferably sulfur trioxide.

In another embodiment of the method, the composition includes a supercritical component in a supercritical state selected from the group of carbon dioxide (CO<sub>2</sub>), ammonia (NH<sub>3</sub>), H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), inert gases (e.g., nitrogen (N<sub>2</sub>), helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe); preferably carbon dioxide.

**10 Brief Description of the Drawing**

Figure 1 is an illustrative representation of a substrate assembly including organic material to be removed in accordance with the present invention.

Figure 2 is a schematic representation of a pressure vessel for use in removal of organic material in accordance with the present invention.

Figure 3 is a schematic representation of an alternate pressure vessel for use in removal of organic material in accordance with the present invention.

**Detailed Description of the Invention**

Supercritical compositions for removal of organic material and methods for using such compositions are described herein. The following description is illustrative of various embodiments of the invention.

As used herein, the term substrate assembly includes a wide variety of structures, e.g., semiconductor-based structures, that can be etched or have organic material or layers that can be removed. A substrate assembly can be a single layer of material, such as, for example, a silicon (Si) wafer, or can include any other number of layers. Substrate assembly is also to be understood as including silicon-on-sapphire (SOS) technology, silicon-on-insulator (SOI) technology, doped and undoped semiconductors, epitaxial layers of silicon (Si) supported by a base semiconductor, as well as other semiconductor-based structures, including any

number of layers as is well known to one skilled in the art. Furthermore, when reference is made to a substrate assembly in the following description, previous process steps may have been utilized to form regions/junctions in a base semiconductor structure. The substrate assembly from which organic material is to be removed can have a patterned mask layer thereon, such as, for example, a patterned resist layer. Yet further, when reference is made to a substrate assembly in the following description, the substrate assembly can be other than a semiconductor-based structure. For example, the substrate assembly may be a structure including one or more layers of other materials, for example, such as glass, tin indium oxide, or other materials used in producing base plates or face plates of flat panel displays. The following detailed description is, therefore, not to be taken in a limiting sense, and the scope of the present invention is defined by the accompanying claims.

A gas enters the supercritical state when the combination of pressure and temperature of the environment in which the gas is contained is above a critical state. For example, the critical temperature of carbon dioxide (CO<sub>2</sub>) is 31°C. The critical pressure of CO<sub>2</sub> is 7.38 MPa (72.8 atmospheres (atm)). When CO<sub>2</sub> is subjected to temperatures and pressures above 31 °C and 7.38 MPa (72.8 atm), respectively, it is in the supercritical state. Further, for example, the critical temperature of sulfur trioxide (SO<sub>3</sub>) is 218.3 °C. The critical pressure of sulfur trioxide is 83.8 atm. When sulfur trioxide is subjected to temperatures and pressures above the critical temperature and pressure, it is in the supercritical state. The critical temperature and pressure of other components is readily calculated or experimentally determined by one skilled in the art.

A gas in the supercritical state is referred to as a supercritical fluid. Supercritical fluids have high solvating capabilities that are typically associated with compositions in the liquid state. Supercritical fluids also have a low viscosity that is characteristic of compositions in the gaseous state. Furthermore, supercritical fluids are able to penetrate (i.e., effectively contact) surfaces better than compositions in

the liquid state.

At least one supercritical component is used in the compositions of the present invention to effectuate the removal of organic material. Supercritical component, as used herein, encompasses all compounds or elements that are present as supercritical fluids.

In one embodiment of a composition for removal of organic material according to the present invention, the supercritical component of the composition includes one or more oxidizer components to effectively remove the organic material. At least one of the oxidizer components must be in a supercritical state.

Generally, the at least one oxidizer component is a strong oxidizing agent (i.e., the oxidizer component is known to oxidize organic material). Preferably, the at least one oxidizer in the supercritical state is an oxidizer component selected from the oxidizers including sulfur trioxide ( $\text{SO}_3$ ), sulfur dioxide ( $\text{SO}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ),  $\text{NO}$ ,  $\text{NO}_2$ , ozone ( $\text{O}_3$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ),  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and oxygen ( $\text{O}_2$ ).

More preferably, the oxidizer component used in the composition for removal of organic material is sulfur trioxide. For example, in a preferred embodiment, the composition used to remove the organic material may be a single supercritical oxidizer component, e.g., sulfur trioxide in a supercritical state.

In an alternate embodiment of a composition for removal of organic material according to the present invention, the composition includes a supercritical fluid mixture of at least one oxidizer component and one or more additional components (i.e., components other than oxidizer components). At least one of the one or more additional components must be in the supercritical state if an oxidizer component is not in the supercritical state. However, both one or more of the oxidizer components and one or more of the other additional components of the supercritical fluid mixture may be in the supercritical state.

Preferably, when the supercritical fluid mixture does not include at least one oxidizer in a supercritical state, at least one of the additional components must be in a supercritical state. In such a supercritical fluid mixture, preferably, the additional

component in a supercritical state is selected from the group of carbon dioxide (CO<sub>2</sub>), ammonia (NH<sub>3</sub>), H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), inert gases (e.g., nitrogen (N<sub>2</sub>), helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), etc.), and similar components, or combinations of the above. Some of the above possible combinations may react to form other active agents (e.g., SO<sub>3</sub> reacts with H<sub>2</sub>O to form H<sub>2</sub>SO<sub>4</sub>).

The use of such additional components in supercritical states to form supercritical fluid mixtures for removal of organic material allow for tailoring the parameters of the removal process, e.g., the temperature and pressure of the supercritical fluid mixture. For example, in one preferred composition, a sulfur trioxide oxidizer component is used in a supercritical fluid of carbon dioxide. The pressure of the system using such a composition can be maintained at a lower state since the critical pressure of carbon dioxide is significantly lower than the supercritical pressure of sulfur trioxide. In this illustrative example of a supercritical fluid mixture including carbon dioxide and sulfur trioxide, the ratio of carbon dioxide:sulfur trioxide is preferably in the range of about 10:1 by volume to about 1:1 by volume. Generally, the ratio of the oxidizer component to the additional component in the supercritical state is in the range of about 1:100 by volume to about 100:1 by volume.

Other additional components may be used to enhance the organic material removal process. Such components may or may not be in a supercritical state. For example, such components may include components, such as inorganic acids (e.g., HCl, HBr, HF), buffering agents (e.g., ammonium fluoride (NH<sub>4</sub>F), tetramethyl ammonium fluoride (Me<sub>4</sub>NF)), surfactants, selectivity enhancers (e.g., tetramethyl ammonium hydroxide (Me<sub>4</sub>NOH), tetramethyl nitrogen fluoride (Me<sub>4</sub>NF), and ammonium fluoride (NH<sub>4</sub>F)), or ligands (e.g., beta-diketones, fluorinated-diketones, organic acids, and the like) to enhance the etching effectiveness or protect other layers of the structure that are present.

One skilled in the art will recognize that the composition may be formed in a

variety of manners and any particular sequence used to attain a composition as described herein is only for illustrative purposes. For example, a supercritical fluid component, e.g., carbon dioxide in the supercritical state, may be added to a supercritical oxidizer component to form a supercritical etching composition; a component not in a supercritical state may be added to a supercritical component either before it is brought to the supercritical state or after it is brought to the supercritical state; a component not in a supercritical state may be provided into an etching chamber while the substrate is being exposed to the supercritical oxidizer component; a supercritical oxidizer component (e.g., SO<sub>3</sub>) may be introduced to the substrate alone, etc.

Further, by varying combinations of pressure and temperature, variable removal characteristics can be obtained. For example, increasing pressure on the supercritical composition causes its density to increase, thus increasing its solvent strength. Increasing the temperature of the supercritical composition normally increases the removal rate of the organic material.

A wide variety of organic materials can be effectively removed using the compositions and methods of the present invention. For example, resist material, photoresist residue, organic residues, carbon-fluorine containing polymers such as those resulting from oxide etching processes or plasma etch processes, and organic impurities from other processes, may be removed according to the present invention. Such compositions and methods are particularly beneficial for removing ion implanted resist, UV hardened resist, X-ray hardened resist and resist in submicrometer grooves or crevices.

Figure 1 is an illustrative representation of a structure 10 including organic material to be removed in accordance with the present invention. As shown in Figure 1, the structure includes a substrate assembly 12 having an additional layer 14, such as an oxide layer, formed thereon. The layer 14 is patterned using a photoresist layer 16 which defines the opening 18 through the layer 14. With the photoresist layer 16 patterned, the opening 18 is etched to surface 20 using a plasma

such as a fluorocarbon or hydrofluorocarbon plasma. As shown in Figure 1, during the etching of the opening 18, organic material, e.g., a nonvolatile polymeric residual layer 21, may be formed on the side walls 19 of the opening 18 being defined. Such organic material 21, in addition to the photoresist layer 16, is removed using a composition 22 according to the present invention prior to other process steps being performed. It will be apparent to one skilled in the art that the structure being formed may be one of any number of different structures. The present invention is not limited to any particular structure described herein. For example, the structure being formed may be part of various devices or circuits, such as SRAMs, DRAMs, flat panel displays, any structure formed with the use of resist material, etc.

The present invention is particularly beneficial for defining structures having critical dimensions of less than 1 micron and preferably any features having a critical dimension of less than or equal to about 0.6 microns, more preferably those features having a critical dimension of less than about 0.25 microns. For example, the present invention is beneficial for removal of organic material in small high aspect ratio features. Small high aspect ratio features are defined herein as features having aspect ratios (i.e., the height to spacing ratio of two adjacent steps of a substrate assembly such as steps which define an opening, a trench, etc.) greater than about 1 and features sizes or critical dimensions of below about 1 micron (e.g., such as opening width (cd) of Figure 1 being less than about 1 micron). Although the present invention is particularly beneficial for definition of such small high aspect ratio features, the removal of organic material from other sized structures is clearly contemplated in accordance with the present invention.

It is desirable to decrease the use of relatively high temperature processing steps for relatively long periods of time. A process sequence in the fabrication of semiconductor integrated circuits (ICs) ideally maintains a relatively low thermal budget. The thermal budget for an IC process sequence is that combination of time and temperature for heat treatments utilized in the fabrication of the IC, above which

electrical performance of the IC is possibly degraded. An IC can only be subjected to a limited number of thermal steps for a limited amount of time before its electrical performance is potentially detrimentally affected. For example, thermal steps often cause dopant gradients at junctions between two regions in an IC to diffuse, such that the potential barrier between the two regions is altered.

Furthermore, thermal steps often cause dopants to migrate into undesired regions, altering device characteristics. For example, because transistors are formed prior to the capacitor in many dynamic random access memory (DRAM) devices, it is desirable to use relatively low temperatures to form the capacitor because higher temperatures cause dopants to diffuse, forming dopant gradients, across the many junctions therein.

Preferably, the temperature range used to remove organic material according to the present invention is in the range of about 30°C to about 250°C. Of course, because at least one component of the composition used to remove the organic material must be in a supercritical state, the temperatures used will need to satisfy the critical temperature requirements for the component which exists in the supercritical state in the composition. For example, relatively low temperatures may be achieved by using carbon dioxide as the supercritical component in the composition. Carbon dioxide has a critical temperature of 31°C. Therefore, use of a CO<sub>2</sub> supercritical component with an oxidizer component (not in a supercritical state) may be used such that thermal budget is conserved. When temperature constraints are not present, for example, such as in early fabrication steps, sulfur trioxide may be used in its supercritical state alone.

Further, preferably, the pressure range used to remove organic material according to the present invention is in the range of about 1 atmosphere to about 250 atmospheres. Of course, because at least one component of the composition used to remove the organic material must be in a supercritical state, the pressure used will need to satisfy the critical pressure requirements for the component which exists in the supercritical state in the composition. By using a supercritical component with a

lower pressure, lower pressure processing parameters can be achieved.

Supercritical etching compositions can be environmentally advantageous over current chemistries, particularly where CO<sub>2</sub> is the primary supercritical component. CO<sub>2</sub> is much less toxic than many standard wafer cleaning compositions. Supercritical fluids also offer high purity when compared to liquid chemical etchants since they are typically purified as gases. Further, supercritical fluids are also capable of being relatively easy to recycle.

Due to the high rate of penetration that is characteristic of supercritical fluids as compared to wet etchants, removal of organic material in accordance with the present invention is more uniform. Uniformity is promoted due to the superior wetting abilities of supercritical compositions, along with their ability to break away material from within etched or partially etched openings of a structure. Another desirable advantage of using supercritical compositions and methods of the present invention is that drying steps are not needed in the IC processing sequence subsequent to an organic material removal step in accordance with the present invention. Elimination of such drying steps contributes to optimizing efficiency in the fabrication of ICs.

The organic material removal process according to the present invention may be employed in batch or continuous processing operational modes. In either case, components of the organic material removal composition are provided to a chamber that includes structures such as that described with reference to Figure 1. The chamber is typically purged prior to providing such components to the chamber, such as with nitrogen or some other inert gas. The flow rate of the components into the chamber will depend on the nature of the organic material removal composition and also on the type and characteristics of the organic material to be removed, e.g., thickness, hardened resist versus ion-implanted resist, etc. The exposure time of the removal composition to structures in the chamber will also vary. A typical time of exposure may be from about 5 seconds to about 10 minutes. Likewise, the removal rate of the organic material will also depend on the nature of the organic material

removal composition and also on the type and characteristics of the organic material to be removed. A typical removal rate may be in the range of about 10 Å/minute to about 1 micron/minute.

According to the present invention, a substrate assembly having organic material that is to be removed (e.g., a semiconductor-based substrate assembly patterned with a photoresist, a base plate of a flat panel display patterned with a photoresist) is exposed to an organic material removal composition according to the present invention and as previously described herein. A preferred process sequence utilizes an apparatus preferably customized for the particular composition. For example, a pressure vessel 114 shown in Figure 2 is a useful tool in which to expose a substrate assembly 116 to the organic material removal composition according to the present invention. The pressure vessel 114 includes a chuck or holder 118 for supporting and/or rotating the substrate assembly 116. Mass or liquid flow controllers 120 operatively attached to the pressure vessel 114 control the input of each component of the composition. For example, an oxidizer component, e.g., sulfur trioxide, and an additional component, e.g., carbon dioxide, each enter the pressure vessel 114 directly through a separate controller 120. It should be understood, however, that an optional apparatus 122 can be used that allows for the mixing of the components prior to their entering the pressure vessel 114 as well as allowing for any number of different components to be mixed.

As illustrated in Figure 2, the components can be pre-mixed in mixing manifold 122. The components can also be heated in the mixing manifold 122 by including heating coils or vanes in walls of manifold 122 to increase heat transfer to the components before passing through an optional circulation heater 124, such as a circulation heater supplied by Watlow Co. of Saint Louis, Missouri. The organic residue removal composition then enters the pressure vessel 114 through a dispensing device 126, such as a shower-head, with at least one of the components in the supercritical state. The circulation heater 124 is preferably used to increase the heating efficiency of the system when creating the supercritical composition in

the mixing manifold 122 prior to entering the pressure vessel 14. The organic material removal composition passes over the substrate 116 from the dispensing device 126.

It is also to be understood that the supercritical etching composition can optionally pass directly over the substrate 116 from a heated transfer line without using a dispensing device 126. Alternatively, each component of the supercritical etching composition can enter the pressure vessel through plumbed supply lines, where the components can then be brought to the supercritical state. The supercritical etching composition is passed over the substrate 116 until the desired organic material is removed.

The pressure vessel 114 also includes a heating mechanism and a pressurization mechanism for controlling the temperature and pressure of the pressure vessel 114. Temperature and pressure within the pressure vessel 114 is at or above the critical temperature and pressure for the components desired to be in a supercritical state. A thermocouple 128 monitors temperature within the pressure vessel 114 and relays an appropriate signal to a temperature control unit 130. The temperature control unit 130 sends appropriate signals to heater inputs 132, which provide heat to the pressure vessel 114. A pressure gauge 134 monitors pressure within the pressure vessel 114 and sends appropriate signals to a pressure control unit 136, which pressurizes/depressurizes the pressure vessel 114. Excess composition is vented or pumped through a vent or pumping system in the direction indicated by arrow 138. For example, the organic material removal composition passes from the pressure vessel 114 to the vent or pumping pressure control system 136 by operation of a pressure differential.

It will be recognized by one skilled in the art that other alternative configurations of tools such as illustrated in Figure 3 can be useful for removing organic material from a substrate assembly 116 using an organic material removal composition according of the present invention. The tool illustrated in Figure 3 is similar to the tool illustrated in Figure 2, but the oxidizing component (prior to

being brought to the supercritical state) first flows from mass or liquid flow controller 140 through circulation heater 124 prior to entering the mixing manifold 122, where any additional components enter through mass or liquid flow controllers 142. When the oxidizer component is capable of etching a particular inorganic material in and of itself, and when using the tool illustrated in Figure 3, other additional components need not be added to the mixing manifold 122 from mass or liquid flow controllers 142.

In one preferred embodiment of the present invention, the organic material removal composition includes only sulfur trioxide in its supercritical state. A pressurizable chamber is heated above the critical temperature (218.3 °C) of sulfur trioxide, preferably below about 250°C. The chamber is then provided with sulfur trioxide at a pressure above the critical pressure (83.8 atmospheres), preferably below about 100 atmospheres. A preferred desired flow of the sulfur trioxide into the pressure chamber is in the range of about 100 sccm to about 1000 sccm. The organic material is removed during a preferred time range of about 10 seconds to about 60 seconds with a removal rate of about 100Å/minute to about 1 micron/minute.

In another preferred embodiment of the present invention, the organic material removal composition includes sulfur trioxide in a nonsupercritical state and carbon dioxide in a supercritical state. A pressurizable chamber is heated above the critical temperature (31 °C) of carbon dioxide, preferably below about 50°C. The chamber is then provided with sulfur trioxide and carbon dioxide at a pressure above the critical pressure (72.8 atmospheres) of carbon dioxide, preferably below about 100 atmospheres. A desired flow of the sulfur trioxide into the pressure chamber is in the range of about 10 sccm to about 200 sccm. A desired flow of the carbon dioxide into the pressure chamber is in the range of about 200 sccm to about 1000 sccm. In other words, the ratio of sulfur trioxide:carbon dioxide is in the range of about 1:1 to about 1:100. The organic material is removed during a time period in the range of about 10 seconds to about 60 seconds with a removal rate of about

10 $\text{\AA}$ /minute to about 1 micron/minute.

All patents, patent applications, and publications disclosed herein are incorporated by reference in their entirety, as if individually incorporated. The foregoing detailed description and illustrations have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom.

5 The invention is not limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the invention defined by the claims.

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What is claimed is:

1. A method for removing organic material in the fabrication of structures, the method comprising:

5 providing a substrate assembly having an exposed organic material; and  
removing at least a portion of the exposed organic material using a  
composition having at least one component in a supercritical state, the composition  
comprising an oxidizer selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur  
dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide  
10 (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>).

15 2. The method of claim 1, wherein the at least one component in a supercritical  
state is an oxidizer selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide  
(SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>,  
Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>).

20 3. The method of claim 2, wherein the at least one component in a supercritical  
state is sulfur trioxide.

4. The method of claim 3, wherein the composition consists essentially of  
sulfur trioxide in the supercritical state.

25 5. The method of claim 1, wherein the composition includes a supercritical  
component in a supercritical state selected from the group of carbon dioxide (CO<sub>2</sub>),  
ammonia (NH<sub>3</sub>), H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), nitrogen (N<sub>2</sub>),  
helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe).

6. The method of claim 5, wherein the supercritical component is carbon  
dioxide and the oxidizer is sulfur trioxide.

7. The method of claim 1, wherein the exposed organic material is selected from the group of resist material, photoresist residue, UV-hardened resist, X-ray hardened resist, carbon-fluorine containing polymers, plasma etch residues, and organic impurities from other processes.

5

8. The method of claim 1, wherein the substrate assembly includes features having aspect ratios greater than about 1 and feature sizes of less than or equal to about 1 micron.

10

9. The method of claim 8, wherein the substrate assembly includes features having aspect ratios greater than about 1 and feature sizes of less than or equal to about 0.25 microns.

15

10. A method for removing an organic material of a substrate assembly, the method comprising:

providing a substrate assembly including an exposed organic material; and exposing the substrate assembly to an oxidizer in a supercritical state, wherein the oxidizer is selected from the group of sulfur trioxide ( $\text{SO}_3$ ), sulfur dioxide ( $\text{SO}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ),  $\text{NO}$ ,  $\text{NO}_2$ , ozone ( $\text{O}_3$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ),  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and oxygen ( $\text{O}_2$ ).

20

11. The method of claim 10, wherein the oxidizer is sulfur trioxide.

25

12. The method of claim 11, wherein the exposed organic material is selected from the group of resist material, photoresist residue, UV-hardened resist, X-ray hardened resist, carbon-fluorine containing polymers, plasma etch residues, and organic impurities from other processes.

13. The method of claim 12, wherein the substrate assembly includes features

having a pitch of less than or equal to about 1 micron.

14. A method for removing an organic material of a substrate assembly, the  
5 method comprising:

providing a substrate assembly including an exposed organic material; and  
exposing the substrate assembly to a composition including an oxidizer and  
at least one supercritical component, wherein the at least one supercritical  
component is selected from the group of carbon dioxide (CO<sub>2</sub>), ammonia (NH<sub>3</sub>),  
10 H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), nitrogen (N<sub>2</sub>), helium (He), neon  
(Ne), argon (Ar), krypton (Kr), and xenon (Xe), and further wherein the oxidizer is  
selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide  
(N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen  
(O<sub>2</sub>).

15. 15. The method of claim 14, wherein the oxidizer is sulfur trioxide.

16. The method of claim 14, wherein the at least one supercritical component is  
carbon dioxide.

20. 17. The method of claim 14, wherein the exposed organic material is selected  
from the group of resist material, photoresist residue, UV-hardened resist, X-ray  
hardened resist, carbon-fluorine containing polymers, plasma etch residues, and  
organic impurities from other processes.

25. 18. The method of claim 14, wherein the substrate assembly includes features  
having aspect ratios greater than about 1 and feature sizes of less than or equal to  
about 1 micron.

19. An organic material removal composition comprising at least one component in a supercritical state, wherein the composition includes an oxidizer selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>).

5

20. The composition of claim 19, wherein the at least one component in a supercritical state is the oxidizer selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>).

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21. The composition of claim 20 wherein the at least one component in a supercritical state is sulfur trioxide.

22. The composition of claim 21, wherein the composition consists essentially of sulfur trioxide in the supercritical state.

15

23. The composition of claim 19, wherein the composition includes a supercritical component in the supercritical state selected from the group of carbon dioxide (CO<sub>2</sub>), ammonia (NH<sub>3</sub>), H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), nitrogen (N<sub>2</sub>), helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe).

20

24. The composition of claim 23, wherein the supercritical component is carbon dioxide and the oxidizer is sulfur trioxide.

25

25. An organic material removal composition comprising an oxidizer in a supercritical state, wherein the oxidizer is selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>).

26. The composition of claim 25, wherein the oxidizer is sulfur trioxide.

27. An organic material removal composition comprising:  
5 a first component selected from the group of carbon dioxide (CO<sub>2</sub>), ammonia (NH<sub>3</sub>), H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), nitrogen (N<sub>2</sub>), helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe), wherein the first component is in a supercritical state; and  
10 a second component selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>).

28. The composition of claim 27, wherein the first component is carbon dioxide.

29. The composition of claim 27, wherein a ratio of the first component to the second component in the supercritical state is in the range of about 1:100 by volume to about 100:1 by volume.

30. The composition of claim 27, wherein the second component is sulfur trioxide and the first component is carbon dioxide.

31. The composition of claim 30, wherein a ratio of carbon dioxide:sulfur trioxide is preferably in the range of about 10:1 by volume to about 1:1 by volume.

32. The composition of claim 30, wherein the sulfur trioxide is in a supercritical state.

33. A method for use in fabricating a semiconductor structure, the method comprising the steps of:  
25 providing a pressurizable chamber;

introducing at least one component of a composition into the chamber;  
positioning a substrate assembly having exposed organic material within the  
chamber;

controlling pressure and temperature of the chamber for maintaining the at least one component of the composition in a supercritical state, the composition comprising an oxidizer selected from the group of sulfur trioxide ( $\text{SO}_3$ ), sulfur dioxide ( $\text{SO}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ),  $\text{NO}$ ,  $\text{NO}_2$ , ozone ( $\text{O}_3$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ),  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and oxygen ( $\text{O}_2$ ); and

removing at least a portion of the organic material from the substrate assembly using the composition having the at least one component in the supercritical state.

34. The method of claim 33, wherein the at least one component in a supercritical state is an oxidizer selected from the group of sulfur trioxide ( $\text{SO}_3$ ), sulfur dioxide ( $\text{SO}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ),  $\text{NO}$ ,  $\text{NO}_2$ , ozone ( $\text{O}_3$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ),  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and oxygen ( $\text{O}_2$ ).

35. The method of claim 34, wherein the at least one component in a supercritical state is sulfur trioxide.

36. The method of claim 35, wherein the composition consists essentially of sulfur trioxide in the supercritical state.

37. The method of claim 33, wherein the composition includes a supercritical component in a supercritical state selected from the group of carbon dioxide (CO<sub>2</sub>), ammonia (NH<sub>3</sub>), H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), nitrogen (N<sub>2</sub>), helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe).

38. The method of claim 37, wherein the supercritical component is carbon

dioxide and the oxidizer is sulfur trioxide.

39. The method of claim 33, wherein the exposed organic material is selected from the group of resist material, photoresist residue, UV-hardened resist, X-ray hardened resist, carbon-fluorine containing polymers, plasma etch residues, and organic impurities from other processes.

40. The method of claim 33, wherein the substrate assembly includes features having aspect ratios greater than about 1 and feature sizes of less than or equal to about 1 micron.

41. A method for use in fabricating a semiconductor structure, the method comprising the steps of:

providing a pressurizable chamber;

positioning a substrate assembly having exposed organic material within the chamber;

introducing sulfur trioxide into the chamber;

controlling pressure and temperature of the chamber for maintaining the sulfur trioxide in a supercritical state; and

removing at least a portion of the remaining organic material from the substrate assembly using the etching composition with the at least one component in the supercritical state.

42. The method of claim 41, wherein the substrate assembly includes a photoresist layer defining features in an underlying layer, wherein the substrate assembly includes features having aspect ratios greater than about 1 and feature sizes of less than or equal to about 1 micron.

**SUPERCRITICAL COMPOSITIONS FOR REMOVAL  
OF ORGANIC MATERIAL AND METHODS OF USING SAME**

**Abstract of the Disclosure**

5 A method for removing organic material in the fabrication of structures includes providing a substrate assembly having an exposed organic material and removing at least a portion of the exposed organic material using a composition having at least one component in a supercritical state. The composition includes an oxidizer selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>),  
10 nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>). For example, the exposed organic material may be selected from the group of resist material, photoresist residue, UV-hardened resist, X-ray hardened resist, carbon-fluorine containing polymers, plasma etch residues, and organic impurities from other processes. The at least one component in a supercritical state may be an oxidizer selected from the group of sulfur trioxide (SO<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), NO, NO<sub>2</sub>, ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), F<sub>2</sub>,  
15 Cl<sub>2</sub>, Br<sub>2</sub>, and oxygen (O<sub>2</sub>); preferably sulfur trioxide. Further, the composition may include a supercritical component in a supercritical state selected from the group of carbon dioxide (CO<sub>2</sub>), ammonia (NH<sub>3</sub>), H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), inert gases (e.g., nitrogen (N<sub>2</sub>), helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe); preferably carbon dioxide. Further, organic material removal compositions for performing such methods are provided.

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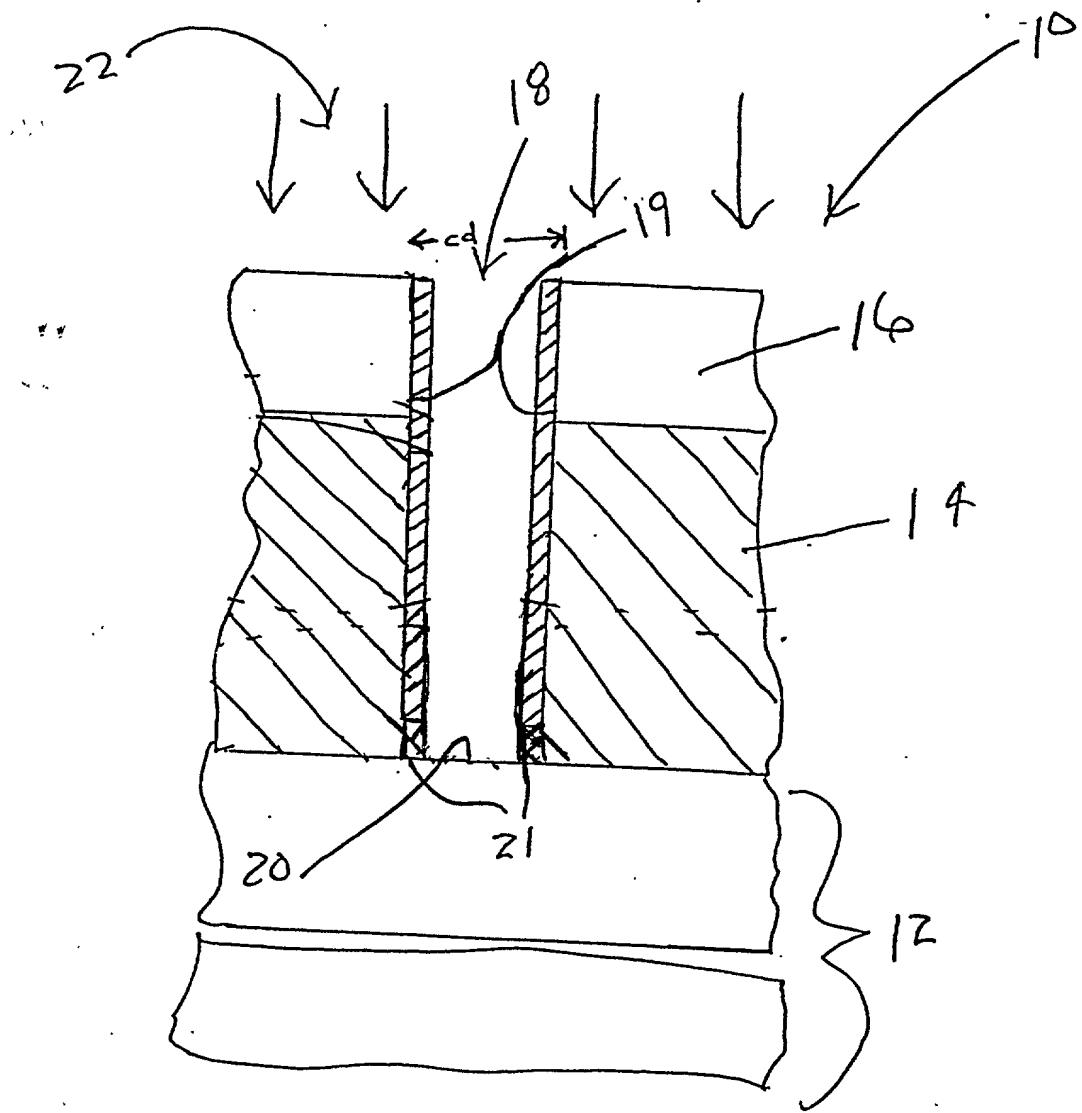
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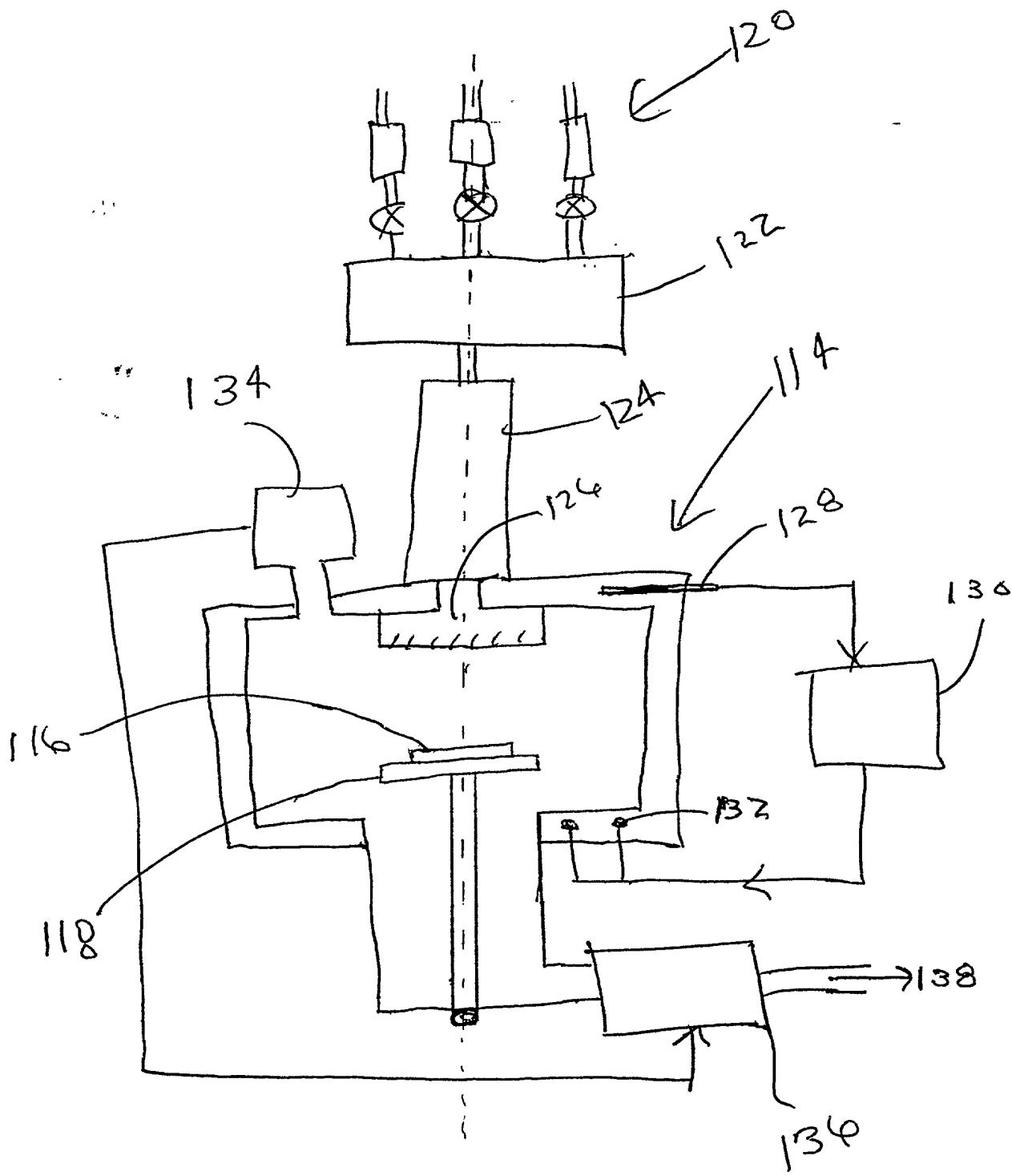
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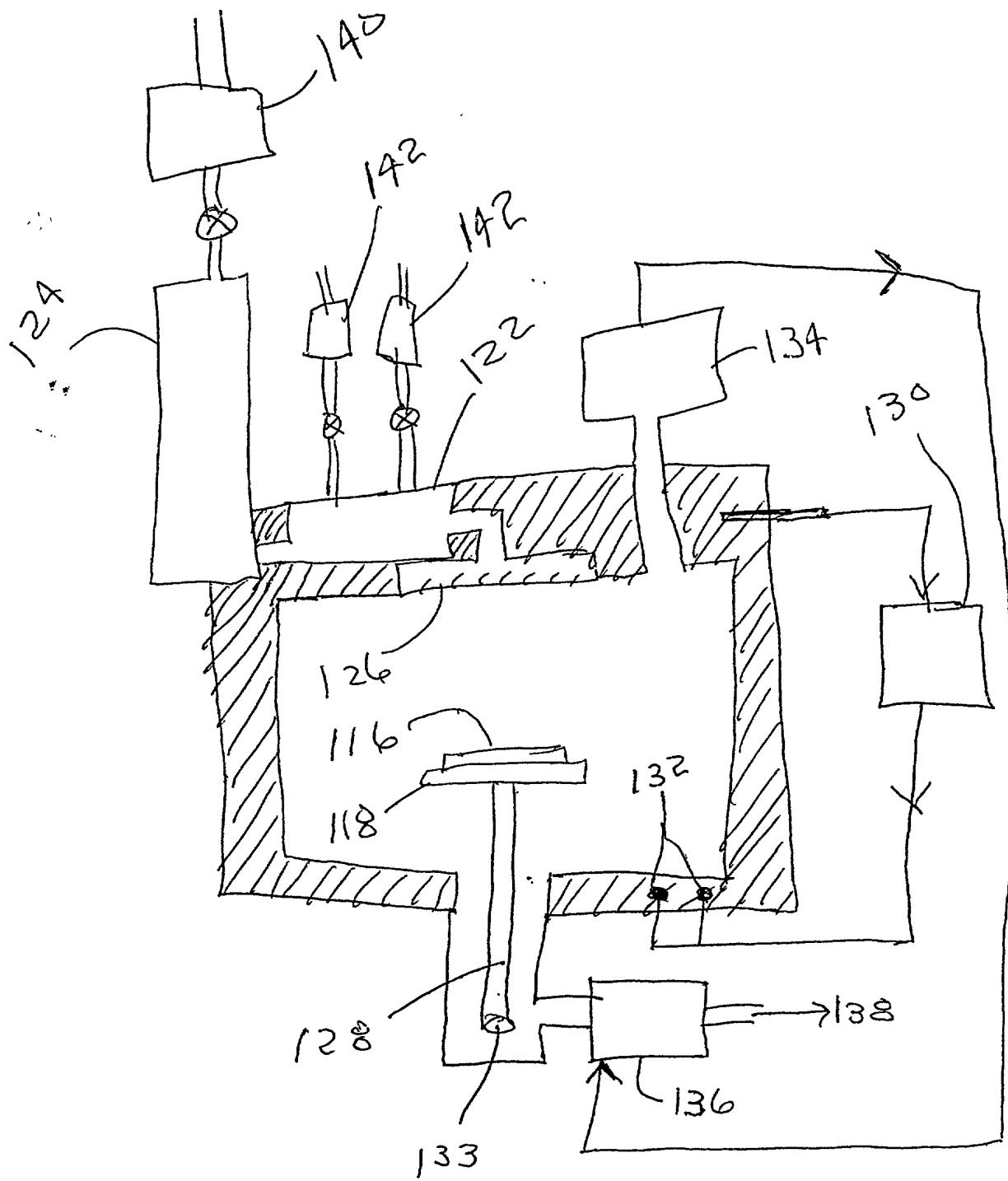
FIGURE 1



## FIGURE 2



### FIGURE 3.



PATENT  
Docket No. 150.00800101

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s):	Vaartstra	)	Group Art Unit: Unknown
Serial No.:	Unassigned	)	Examiner: Unknown
Filed:	Herewith	)	
For:	<u>SUPERCritical COMPOSITIONS FOR REMOVAL OF ORGANIC MATERIAL AND METHODS OF USING SAME</u>		

ELECTION UNDER 37 C.F.R. §§3.71 AND 3.73 AND POWER OF ATTORNEY

Assistant Commissioner for Patents  
Washington, D.C. 20231

Dear Sir:

The undersigned, being Assignee of the entire interest in the above-identified application by virtue of an Assignment recorded in the United States Patent and Trademark Office as set forth below or filed herewith, hereby elects, under 37 C.F.R. §3.71, to prosecute the application to the exclusion of the inventor(s).

The Assignee hereby revokes any previous Powers of Attorney and appoints: Ann M. Mueting (Reg. No. 33,977); Kevin W. Raasch (Reg. No. 35,651); Mark J. Gebhardt (Reg. No. 35,518); Amelia A. Buhain (Reg. No. 38,835); Victoria A. Sandberg (Reg. No. 41,287); Mark A. Hollingsworth (Reg. No. 38,491); Paul B. Simboli (Reg. No. 38,616); David L. Provence (Reg. No. 43,022); Lia M. Pappas (Reg. No. 34,095); W. Eric Webstad (Reg. No. 35,406); Walter M. Fields (Reg. No. 37,130); Charles B. Brantley, II (Reg. No. 38,086); Susan B. Collier (Reg. No. 34, 566); Kevin D. Martin (Reg. No. 37,882); and David J. Paul (Reg. No. 34,692)

as its attorney or agent (with full powers of appointment, substitution, and revocation) to prosecute the application, and any division, continuation, continuation-in-part, reexamination, or reissue thereof, to make alterations and amendments therein, and to transact all business in the Patent and Trademark Office in connection therewith, and to receive any Letters Patent.

Pursuant to 37 C.F.R. §3.73, the undersigned certifies that the evidentiary documents have been reviewed, specifically the Assignment to Micron Technology, Inc. referenced below, and certifies that to the best of my knowledge and belief, title remains in the name of the Assignee.

Please direct all communications as follows:

Attention: Ann M. Mueting  
Mueting, Raasch & Gebhardt, P.A.  
P.O. Box 581415  
Minneapolis, MN 55458-1415  
Telephone No. (612) 305-1217

ASSIGNEE: Micron Technology, Inc.

Date: 8/28/98

By: MLL

Name: Michael L. Lynch  
Title: Chief Patent Counsel

ASSIGNMENT:

Concurrently filed herewith for recording, a copy of which is attached hereto.  
 Previously recorded on: \_\_\_\_\_, at Reel: \_\_\_\_\_ Frame: \_\_\_\_\_

Docket 150.00800101

**DECLARATION**

I, Brian A. Vaartstra, declare that: (1) my citizenship and mailing address are indicated below; (2) I have reviewed and understand the contents of the specification identified below, including the claims, as amended by any amendment specifically referred to herein, (3) I believe that I am the original and first inventor of the subject matter in

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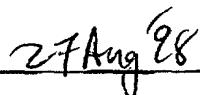
described and claimed therein and for which a patent is sought; and (4) I hereby acknowledge my duty to disclose to the Patent and Trademark Office all information known to me to be material to the patentability as defined in Title 37, Code of Federal Regulations, §1.56.\*

The undersigned declares further that all statements made herein of his/her own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Wherefore, I pray that Letters Patent be granted to me for the invention described and claimed in the specification identified above and I hereby subscribe my name to the foregoing specification and claims, Declaration and Power of Attorney, on the date indicated below.

  
\_\_\_\_\_  
Name: Brian A. Vaartstra  
Citizenship: Canada  
Address: 3417 Braden Lane  
\_\_\_\_\_  
Nampa, ID 83686

Date



§ 1.56 Duty to disclose information material to patentability.

(a) A patent by its very nature is affected with a public interest. The public interest is best served, and the most effective patent examination occurs when, at the time an application is being examined, the Office is aware of and evaluates the teachings of all information material to patentability. Each individual associated with the filing and prosecution of a patent application has a duty of candor and good faith in dealing with the Office, which includes a duty to disclose to the Office all information known to that individual to be material to patentability as defined in this section. The duty to disclose information exists with respect to each pending claim until the claim is cancelled or withdrawn from consideration, or the application becomes abandoned. Information material to the patentability of a claim that is cancelled or withdrawn from consideration need not be submitted if the information is not material to the patentability of any claim remaining under consideration in the application. There is no duty to submit information which is not material to the patentability of any existing claim. The duty to disclose all information known to be material to patentability is deemed to be satisfied if all information known to be material to patentability of any claim issued in a patent was cited by the Office or submitted to the Office in the manner prescribed by §§ 1.97(b)-(d) and 1.98. However, no patent will be granted on an application in connection with which fraud on the Office was practiced or attempted or the duty of disclosure was violated through bad faith or intentional misconduct. The Office encourages applicants to carefully examine:

- (1) Prior art cited in search reports of a foreign patent office in a counterpart application, and
- (2) The closest information over which individuals associated with the filing or prosecution of a patent application believe any pending claim patentably defines, to make sure that any material information contained therein is disclosed to the Office.

(b) Under this section, information is material to patentability when it is not cumulative to information already of record or being made of record in the application, and

- (1) It establishes, by itself or in combination with other information, a prima facie case of unpatentability of a claim; or
- (2) It refutes, or is inconsistent with, a position the applicant takes in:
  - (i) Opposing an argument of unpatentability relied on by the Office, or
  - (ii) Asserting an argument of patentability.

A prima facie case of unpatentability is established when the information compels a conclusion that a claim is unpatentable under the preponderance of evidence, burden-of-proof standard, giving each term in the claim its broadest reasonable construction consistent with the specification, and before any consideration is given to evidence which may be submitted in an attempt to establish a contrary conclusion of patentability.

(c) Individuals associated with the filing or prosecution of a patent application within the meaning of this section are:

- (1) Each inventor named in the application;
- (2) Each attorney or agent who prepares or prosecutes the application; and
- (3) Every other person who is substantively involved in the preparation or prosecution of the application and who is associated with the inventor, with the assignee or with anyone to whom there is an obligation to assign the application.

(d) Individuals other than the attorney, agent or inventor may comply with this section by disclosing information to the attorney, agent, or inventor.